

# PATENT ABSTRACTS OF JAPAN

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## (54) CURABLE COMPOSITION

### (57)Abstract:

PURPOSE: To obtain a curable composition lowered in viscosity without lowering its flexibility.

CONSTITUTION: 100 pts.wt. polyoxypropylene polymer containing 2.4 hydrolyzable silicon groups on the average per molecular chain and having a molecular weight of 30000 and its polymer is mixed with 30 pts.wt. low-molecular compound containing 0.5 to below 1.5 hydrolyzable silicon groups, having a molecular weight of 2200-3200 and having a main chain comprising a polyether. Because it contains lowly migrating additives, it does not cause staining around the sealed part and does not adversely affect adhesiveness when it is used as a sealing agent or the like.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the room-temperature-curing nature constituent hardened under hygroscopic-moisture existence.

[0002]

[Description of the Prior Art] The approach of making harden various kinds of compounds which have an end hydrolysis nature silicon radical until now, and using it for a sealing material, adhesives, etc. is learned well, and is a useful approach industrially.

[0003] The compound especially whose principal chain is a polyether among such compounds is liquefied at a room temperature, and when a hardened material holds flexibility also at low temperature comparatively and uses for a sealing material, adhesives, etc., it is equipped with the desirable property.

[0004] As resin of such hygroscopic-moisture hardenability, the resin of the hygroscopic-moisture hardenability which has a hydrolysis nature silicon radical is raised to the end indicated by JP,3-72527,A, JP,3-47825,A, etc. With the compound which has a hydrolysis nature machine at such the end, although the flexibility of a hardened material increases, the viscosity of resin will become high and workability will get remarkably bad, so that the molecular weight is generally large.

[0005] Moreover, although viscosity will become low if the molecular weight of such a compound is small, a hardened material will become a thing inferior to flexibility. In order to consider as hypoviscosity, maintaining the flexibility of a hardened material until now, various kinds of plasticizers have been used.

[0006] As such a plasticizer, aromatic series carboxylate, aliphatic series carboxylate, glycol ester, phosphoric ester, an epoxy plasticizer, chlorinated paraffin, etc. are used. However, since these plasticizers are translatable, when it is used for a sealing agent etc., they have the fault of doing contamination of the sealing section circumference, and the bad influence to an adhesive property.

[0007]

[Problem(s) to be Solved by the Invention] Then, as a result of being able to reduce the viscosity of a resin constituent and examining the very low additive of translatability moreover to the resin of the hygroscopic-moisture hardenability which has a hydrolysis nature silicon radical, without reducing the flexibility, it resulted in this invention.

[0008]

[Means for Solving the Problem] Namely, the macromolecule polymer (I) of the hydrolysis nature silicon radical content of molecular weight 8000-50000 which averages to a chain and has 1.5 or more hydrolysis nature silicon radicals, and its polymer 100 weight section are received. The room-temperature-curing nature constituent which contains the 1 - 200 weight section for the low molecular weight compound (II) of the hydrolysis nature silicon radical content whose with a molecular weight of less than 300 to 8000 which averages to a chain and has less than 0.5 to 1.5 hydrolysis nature silicon radical principal chain is a polyether is offered.

[0009] The macromolecule polymer (I) of the hydrolysis nature silicon radical content used by this

invention is a compound which averages to a chain, has 1.5 or more hydrolysis nature silicon radicals, and is hardened at the bottom room temperature of hygroscopic-moisture existence of molecular weight 8000-50000, and it is desirable that especially a principal chain essentially consists of a polyether.

[0010] The macromolecule polymer (I) of hydrolysis nature silicon radical content of this invention is obtained by introducing an end hydrolysis nature silicon radical by the suitable approach for the compound known as the polyether and polyol of an end hydroxyl group.

[0011] Such a polymer is proposed by JP,3-47825,A, JP,3-72527,A, JP,3-79627,A, JP,46-30711,B, JP,45-36319,B, JP,46-17553,B, etc.

[0012] The macromolecule polymer (I) of hydrolysis nature silicon radical content introduces a hydrolysis nature silicon radical into the end of the polyether compound which has a functional group so that it may state below, and is manufactured.

[0013] A polyether compound has the desirable thing of the hydroxyl-group end which mono-epoxide, such as alkylene oxide, etc. is made to react to initiators, such as a hydroxy compound which has at least one hydroxyl group under existence of catalysts, such as an alkali-metal catalyst, a compound metallocyanide complex compound catalyst, and metalloporphyrin, and is manufactured. As for the number of functional groups of a polyether compound, two or more are desirable, and 2 or 3 are especially desirable.

[0014] As a polyether compound, a polyoxyethylene, polyoxypropylene, a polyoxy butylene, polyoxy hexylene, polyoxy tetramethylen, and these copolymerization objects are specifically raised.

[0015] Especially desirable polyether compounds are polyoxypropylene diol and polyoxypropylene triol. Moreover, when using for following (1) or the approach of (4), the polyether compound of olefin ends, such as allyl compound end polyoxypropylene mono-oar, can also be used.

[0016] As a hydrolysis nature silicon radical of this invention, the hydrolysis nature silicon radical generally known that what is necessary is just the silicon radical in which hydrolysis and crosslinking reaction occur with hygroscopic moisture can be used.

[0017] For example, the silyl radical expressed with a general formula (A) is good.

- SiXa R3-a ... (A)

[0018] The inside R of a formula is the permutation of carbon numbers 1-20, or an unsubstituted univalent organic radical, and is a with a carbon number of eight or less alkyl group, a phenyl group, and a fluoro alkyl group preferably. They are a methyl group, an ethyl group, a propyl group, butyl, a hexyl group, a cyclohexyl radical, a phenyl group, etc. especially preferably.

[0019] X is a hydrolysis nature machine, for example, has a halogen atom, an alkoxy group, an acyloxy radical, an amide group, the amino group, an amino oxy-radical, a KETOKISHI mate radical, an acid-amide radical, a hydride radical, etc.

[0020] As for the carbon number of the hydrolysis nature machine which has a carbon atom among these, six or less are desirable, and four especially or less are desirable. A desirable hydrolysis nature machine can illustrate a with a carbon number of four or less lower alkoxy group especially a methoxy group and an ethoxy radical, a propoxy group, a propenyl radical, etc. a is 1, 2, or 3 and it is desirable that it is especially 2 or 3.

[0021] Although especially the approach of the installation to the polyether compound of the silyl radical shown by the general formula (A) is not limited, it can be introduced, for example by the following approaches.

[0022] (1) The approach to which the hydrosilyl compound expressed in the end of the polyether compound which has a functional group as what introduced the olefin radical by the general formula (B) is made to react.

HSiXa R3-a ... (B)

(It is the same as the above the inside R, X, and a of a formula)

[0023] The compound which has a partial saturation radical and a functional group is made to react to the end hydroxyl group of a polyether compound as an approach of introducing an olefin radical here, and in case the polymerization of the approach of combining by ether linkage, the ester bond, the urethane bond, carbonate association, etc. or the alkylene oxide is carried out, the approach of

introducing an olefin radical into a side chain etc. is mentioned by adding and carrying out copolymerization of the olefin radical content epoxy compounds, such as allyl glycidyl ether.

[0024] (2) The approach to which the compound expressed with the end of the polyether compound which has a functional group by the general formula (C) is made to react.

R3-a-SiXa-R1 NCO ... (C)

(It is the same as the above the inside R, X, and a of a formula.) R1 Divalent hydrocarbon group of carbon numbers 1-17.

[0025] (3) How to make W sets of a silicon compound expressed with a general formula (D) react to this isocyanate radical after making the poly isocyanate compounds, such as tolylene diisocyanate, react to the end of the polyether compound which has a functional group and considering as an isocyanate radical end.

[0026] R3-a-SiXa-R1 W ... (D)

(The inside R and R1 of a formula, X, and a are the same as the above.) W is a hydroxyl group, a carboxyl group, a sulphydryl group, and the active hydrogen content radical amino-group (the 1st class or the 2nd class) - Selected.

[0027] (4) The approach to which introduce an olefin radical into the end of the polyether compound which has a functional group, and the olefin radical and the sulphydryl group of a silicon compound expressed with the general formula (D) whose W is a sulphydryl group are made to react.

[0028] hydrolysis nature silicon -- the base -- the inside of the chain of the macromolecule polymer (I) of hydrolysis nature silicon radical content -- averaging -- 1.5-8 -- it is desirable that it is especially 1.6-4.

[0029] As a macromolecule polymer (I) of hydrolysis nature silicon radical content of this invention, the organic polymer of molecular weight 8000-50000 can be used. It becomes what has the elongation of a hardened material low especially when the molecular weight of this organic polymer has molecular weight lower than 8000, and when molecular weight is 50000 or more, workability gets remarkably bad for hyperviscosity. But desirable molecular weight is 10000-40000.

[0030] In this invention, to the macromolecule polymer (I) of the above-mentioned hydrolysis nature silicon radical content, it averages to a chain, and has less than 0.5 to 1.5 hydrolysis nature silicon radical, and the low molecular weight compound (II) of the hydrolysis nature silicon radical content whose principal chain is a polyether is used as the reactant adhesiveness-reducing agent and plasticizer of non-translatability.

[0031] As a process of the low molecular weight compound (II) of such hydrolysis nature silicon radical content, ring opening polymerization of alkylene oxide is performed using the initiator of one organic functions, and it considers as polyether mono-oar, and manufactures after that by the approach of changing a hydroxyl group into a hydrolysis nature silicon radical by the approach of aforementioned (1) - (4) etc.

[0032] this polyether mono-oar -- the alcohol of the aliphatic series of carbon numbers 1-20, an alicycle group, and aromatic series, a thioalcohol, secondary amine, a carboxylic acid, etc. -- an initiator -- carrying out -- the above -- by the well-known approach, ring opening polymerization of the alkylene oxide is carried out, and it is obtained.

[0033] When introducing a hydrolysis nature silicon radical by the above (1) and the approach of (4), the polyether mono-oar which manufactured as an initiator the mono-oar which has partial saturation radicals, such as allyl alcohol, may be used, and that end hydroxyl group may be changed into an inactive organic radical by the approach of making it react with a benzoyl chloride etc. in this case.

[0034] the hydrolysis nature in the low molecular weight compound (II) of the hydrolysis nature silicon radical content used by this invention -- the base is averaged in a chain, and is 0.5 to less than 1.5, and especially 0.5-1.2 are desirable.

[0035] As molecular weight of the low molecular weight compound (II) of the hydrolysis nature silicon radical content used by this invention, 300 to less than 8000 are desirable. When the molecular weight of this compound is 8000 or more, since the effectiveness as an adhesiveness-reducing agent becomes low, it is not desirable. Especially 300-6000 are desirable. But desirable molecular weight is 2000-4000.

[0036] In this invention, 1-200 weight section use of the low molecular weight compound (II) of hydrolysis nature silicon radical content is carried out to the macromolecule (polymer I) 100 weight section of hydrolysis nature silicon radical content. The 1 - 100 weight section, especially 1 - 80 weight section are preferably desirable.

[0037] In the constituent of this invention, if required for well-known various curing catalysts, a bulking agent, and an additive pan, a plasticizer etc. can be included.

[0038] As a curing catalyst, various kinds of metaled carboxylate, acetylacetone complex, acetoacetic-acid esthetic rate complex, various kinds of acids, and base matter can be used. Specifically, metal salts, such as octylic acid tin, lead octylate, and a dialkyl tin dicarboxylic acid salt, dibutyltin bisacetylacetone, an organic amine, etc. are raised. these catalysts are independent -- or it can be used together and used.

[0039] A fibrous bulking agent like bulking agents, such as a fumes silica, a sedimentation nature silica, a silicic anhydride, water silicic acid and a bulking agent like carbon black, a calcium carbonate, a magnesium carbonate, the diatom earth, baking clay, clay, talc, titanium oxide, a bentonite, organic bentonite, ferric oxide, a zinc oxide, an active white, hydrogenation castor oil, and milt balun, asbestos, a glass fiber, and a filament as a bulking agent can be used.

[0040] as a plasticizer -- aliphatic series carboxylate [, such as phthalic ester; dioctyl adipates, such as dioctyl phthalate, dibutyl phthalate, and butylbenzyl phthalate, succinic-acid isodecyl, a dibutyl sebacate, and butyl oleate, ]; -- epoxy plasticizer; chlorinated paraffin, such as phosphoric ester; epoxidized soybean oil, such as glucohol ester; trioctyl phosphate, such as pentaerythritol ester, and tricresyl phosphate, and epoxy stearic acid benzyl, etc. can use it with independent or two or more sorts of mixture.

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[0041] As an additive, adhesion grant agents, such as phenol resin and an epoxy resin, a pigment, various kinds of antioxidants, an ultraviolet ray absorbent, etc. are raised. Especially the room-temperature-curing nature resin constituent of this invention can be used as the object for elastic sealants, and an object for adhesives.

[0042]

[Example] Although the example of this invention is raised to below, it is not limited to these. After having made propylene oxide react to the bottom of compound metallocyanide complex compound catalyst existence by the approach given in JP,3-72527,A by having made [example 1 of reference] 2-ethylhexanol into the initiator, having manufactured polyoxypropylene mono-oar, making the allyl chloride react subsequently to an end hydroxyl group and introducing a partial saturation radical, methyl dimethoxysilane was made to react further, a principal chain is polyoxypropylene and the additive A of the molecular weight 3200 which has a methyl dimethoxy silyl propyl group was compounded as an end group. The viscosity of Additive A was 620cps at 25 degrees C.

[0043] Carried out ring opening polymerization of the bottom propylene oxide of existence of a compound metallocyanide complex compound catalyst by having made [example 2 of reference] 2-ethylhexanol into the initiator, considered as the polyoxypropylene mono-oar of molecular weight 3000, it was made to react with the methyl dimethoxy silyl propyl isocyanate of equimolar to this mono-oar further, and Additive B was compounded. The viscosity of Additive B was 750cps at 25 degrees C.

[0044] Ring opening polymerization of the propylene oxide is carried out by making [example 3 of reference] allyl alcohol into an initiator, and it considers as the polyoxypropylene mono-oar of piece end allyloxy radical content of molecular weight 2000, and it was made to react with a hydroxyl group and the benzoyl chloride of equimolar under triethylamine existence continuously. The reaction mixture was diluted with the hexane of an amount 5 times, and was rinsed, except for the triethylamine hydrochloride, the hexane was distilled off and one end acquired the monoallyl object of a benzoyloxy radical. Next, with the conventional method, it was made to react with methyl dimethoxysilane by having made chloroplatinic acid into the catalyst, the allyl group was changed into the methyl dimethoxy silyl propyl group, and the additive C of molecular weight 2200 was compounded. The viscosity of Additive C was 700cps at 25 degrees C.

[0045] A [examples 1-3] glycerol An initiator It carries out. The bottom propylene oxide of existence of

a compound metallocyanide complex compound catalyst As opposed to the silyl radical content polyoxypropylene polyether compound 100 weight section of the molecular weight 30000 which introduced an average of 2.4 methyl dimethoxy silyl propyl groups per molecule into the end of the polyoxypropylene triol which was made to react and was obtained The phenolic antioxidant 1 weight section is added as the dibutyltin dilaurate 1 weight section and an additive by making additive A-C into 30 weight sections and a curing catalyst. It considered as uniform mixture and the weight change (weight percentage reduction) when dipping the viscosity before hardening, the physical properties after hardening (50% modulus, breaking strength, elongation), and a hardened material in a solvent was measured.

[0046] The same examination as examples 1-3 was performed about the thing containing dioctyl phthalate (DOP) as the thing which does not contain an additive instead of and an additive in the [examples 4-5 of comparison] examples 1-3. [ additive A-C ] The obtained result is shown in Table 1.

[0047]

[Table 1]

	例1	例2	例3	例4	例5
添加剤	A	B	C	なし	DOP
粘度 (c p s, 25°C)	25000	27000	26500	37000	24000
モジュラス(kg/cm <sup>2</sup> ) <sup>#1</sup>	0.78	0.81	0.84	1.50	0.75
破断強度(kg/cm <sup>2</sup> ) <sup>#1</sup>	4.2	4.5	4.8	6.2	4.8
伸び(%) <sup>#1</sup>	580	560	520	400	620
重量減少率(%) <sup>#2</sup>	8	10	10	6	28
# 1 : 2 mm厚シート物性 (J I S 3号ダンベル)					
# 2 : 硬化物 1.0 g をテトラヒドロフラン 100 cm <sup>3</sup> に 25°C で 24 時間攪拌しながら浸漬し、取り出した後、減圧下で 乾燥した時の試験前の重量と比較した重量減少率を示す。					

[0048]

[Effect of the Invention] The viscosity of a resin constituent can be reduced without reducing the flexibility by this invention to the resin of the hygroscopic-moisture hardenability which has a hydrolysis nature silicon radical. And since the additive used by this invention has very low translatability, when the constituent of this invention is used for a sealing agent etc., it does neither contamination of the sealing section circumference, nor the bad influence to an adhesive property.

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**CLAIMS**

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**[Claim(s)]**

[Claim 1] The room-temperature-curing nature constituent which contains the 1 - 200 weight section for the low molecular weight compound (II) of the hydrolysis nature silicon radical content whose with a molecular weight of less than 300 to 8000 which averages to a chain and has less than 0.5 to 1.5 hydrolysis nature silicon radical to the macromolecule polymer (I) of the hydrolysis nature silicon radical content of molecular weight 8000-50000 which averages to a chain and has 1.5 or more hydrolysis nature silicon radicals, and its polymer 100 weight section principal chain is a polyether.

[Claim 2] The room-temperature-curing nature constituent of claim 1 whose principal chain of a macromolecule polymer (I) is essentially a polyether.

[Claim 3] The room-temperature-curing nature constituent of claim 1 in which a macromolecule polymer (I) and the hydrolysis nature silicon radical of a low molecular weight compound (II) are shown by the following general formula.

- SiX<sub>a</sub> R<sub>3-a</sub> ... (A)

(As for the inside R of a formula, the permutation of carbon numbers 1-20 or an unsubstituted univalent organic radical, and X show a hydrolysis nature silicon radical, and a shows 1, 2, or 3.)

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[Translation done.]